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SYNTHESIS AND STRUCTURE OF HEXAMOLYBDOBISORGANOARSONATES. (U)

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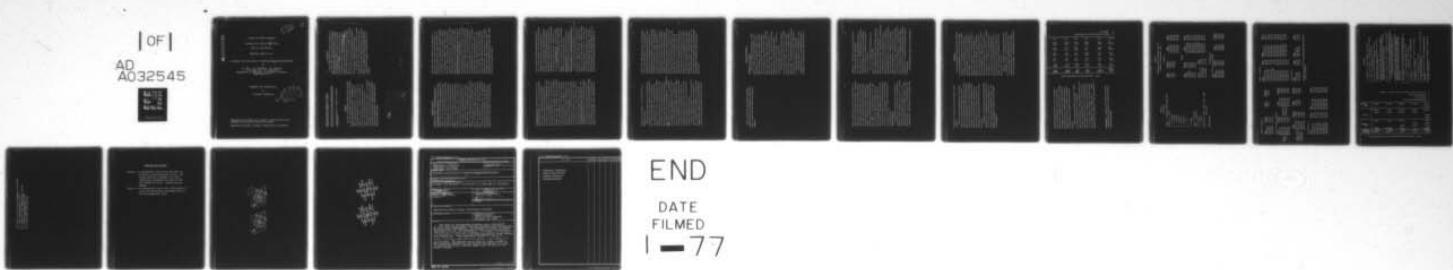
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Office of Naval Research

Contract No. N00014-75-C-0945

Task No. NR 053-576

Technical Report No.6

Synthesis and Structure of Hexamolyb**do**bisorganoarsonates

by

W. Kwak, L.M. Rajdović, J.K. Stalick,

M.T. Pope\* and C.O. Quicksall\*

Department of Chemistry, Georgetown University  
Washington, D.C.



Prepared for Publication

in

Inorganic Chemistry



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Contribution from the Department of Chemistry,  
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Synthesis and Structure of Hexamolybdoisorganoarsenates

M. Kwak, L.M. Rajkovich, J.K. Stalick, M.T. Pope\* and  
C.O. Quicksall\*

Abstract

Five salts of the heteropoly molybdate anion  $(RAs)_2Mo_6O_{24}^{2-}$ , ( $R = \text{CH}_3, \text{C}_6\text{H}_5$ , and  $\text{P}^{\bullet}\text{C}_6\text{H}_5\text{NH}_2$ ) have been synthesized and characterized by spectroscopic measurements. The complexes are stable in aqueous solutions at pH 3-5. The structure of  $[(\text{CH}_3)_2\text{Na}_2(\text{CH}_3\text{As})_2\text{Mo}_6\text{O}_{24}] \cdot 6\text{H}_2\text{O}$  ( $\text{PI}$ ;  $a = 11.712(2)$ ,  $b = 11.589(1)$ ,  $c = 8.331(1)$ ,  $\alpha = 87.84(1)^\circ$ ,  $\beta = 110.31(1)^\circ$ ,  $\gamma = 112.13(1)^\circ$ ) has been determined by single crystal X-ray diffraction. Final consistency indices of 0.043 ( $R_1 = r(|F_O| - |F_C|)/r|F_O|$ ) and 0.072 ( $R_2 = [Iw(|F_O| - |F_C|)^2/Iw|F_O|^2]^{1/2}$ ) were obtained. The structure of the anion is closely related to that previously reported for  $(\text{CH}_3\text{P})_2\text{Mo}_6\text{O}_{24}^{2-}$  and consists of a ring of six edge-shared  $\text{MoO}_6$  octahedra capped above and below by the  $\text{CH}_3\text{AsO}_4^{2-}$  groups.

Introduction

As part of our program to investigate the chemistry of organic derivatives of heteropolyoxometallate complexes we have previously described molybdenum complexes of monoalkyl- and arylphosphonates,  $\text{RPO}_3^{2-}$ , and dialkyl- and arylarsinates  $\text{R}_2\text{AsO}_4^{2-}$ . We now report the synthesis, solution properties and structure of a series of polymolybdate anions based on monoalkyl- and arylarsenates  $\text{RAsO}_4^{2-}$ . In 1913 Rosenthal and Bielecki isolated organic derivatives of this type with  $\text{RAsO}_4^{2-}$ :

$\text{MoO}_3$  ratios of 1:3, 1:6, 1:9 and 2:9. In addition, the existence of 2:2, 2:5 and 1:9 complexes of methylarsenate and molybdate have been claimed on the basis of solution studies.<sup>2,3</sup> We have prepared several examples of two series of complexes with the As:Mo ratio 1:3 and in this paper we describe those complexes with the general formula  $(RAs)_2\text{Mo}_6\text{O}_{24}^{2-}$ . Very recently Pilowitz and Klempner<sup>4</sup> have reported the phenyl derivative of this series and proposed its structure from the  $^{17}\text{O}$  spectrum.

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#### Experimental Section

##### Preparation of Complexes: Hexamolybdatebis(methylarsonate),

Tetramethylammonium-sodium double salt.--A solution of sodium molybdate (21.8 g, 0.09 mol) and sodium methylarsonate<sup>5</sup> (5.6 g, 0.03 mol) in 50 ml of water was adjusted to pH 5 with dilute sulfuric acid. After the solution had been boiled for 20 min., tetramethylammonium chloride (6.6 g, 0.06 mol) was dissolved in the warm solution. The pH of the resulting solution was adjusted to 5 with dilute sulfuric acid and then boiled for another 10 min. The hot solution was filtered and allowed to evaporate at room temperature. Traces of a mixture of white and yellow material were removed by filtration and in a few days a large number of tiny colorless crystals started to appear. As they were allowed to grow for another few days, large colorless blocks (or sometimes white powder) began to separate. After several days the well-shaped colorless crystals were mechanically separated from the chunky blocks<sup>6</sup> (or white powder). The crystals were dipped in cold water, washed with cold water on a Buchner funnel with suction, and then dried in the air. The yield was 9.3 g, i.e. 44%, based on the molecular formula  $(\text{CH}_3)_4\text{N}^+ \text{Na}_2 (\text{CH}_3\text{As})_2\text{Mo}_6\text{O}_{14} \cdot 6\text{H}_2\text{O}$ . The preparation of this salt was not always reproducible and other salts of the heteropoly anion were not obtained. The crude product was dissolved in 60 ml of hot water. After filtration the clear

solution was allowed to evaporate at room temperature. A small amount of yellow material which formed overnight was filtered off and the pH of the filtrate was adjusted to 4.5 by the dissolution of a small amount of solid sodium molybdate in the filtrate. When the solution was allowed to evaporate at room temperature, transparent crystals started to separate in two days. After four days the crystals were collected by filtration and washed with cold water. The transparent crystals became opaque rapidly and finally pulverized upon air-drying. Analytical data for all the new compounds are given in Table I.

Hexamolybdatebisphenylarsonate, Guanidinium salt.--Phenylarsonic acid (4.1 g, 0.02 mol) and sodium molybdate (15.5 g, 0.064 mol) were dissolved successively in ca. 70 ml of water. The slightly cloudy solution was adjusted to pH 4 with dilute sulfuric acid and then boiled for 30 min. The hot solution was filtered and to the filtrate was added 200 ml of pH 4 solution containing guanidinium hydrochloride (3.8 g, 0.04 mol). A small amount of white powder formed, which redissolved upon heating. The solution was boiled to reduce its volume to ca. 150 ml and kept at 5°C overnight. White needles, slightly contaminated with some brown powder separated and were filtered off and washed with pH 4 water. The yield was 9 g, i.e. 57%, based on the molecular formula  $\text{C}(\text{NH}_2)_3 \cdot ((\text{C}_6\text{H}_5\text{As})_2\text{Mo}_6\text{O}_{14}) \cdot 4\text{H}_2\text{O}$ . The crude product was recrystallized rapidly from hot water, washed with pH 4 water and dried in the air.

Tetramethylammonium salt.--Phenylarsonic acid (0.8 g, 0.04 mol) and sodium molybdate (29.1 g, 0.12 mol) were dissolved in 130 ml of water. The resulting solution was adjusted to pH 4.7 with dilute sulfuric acid and boiled for 30 min. After cooling to room temperature, tetramethylammonium chloride (6.6 g, 0.06 mol) dissolved in 20 ml of water was added. The final solution was readjusted to pH 4.7 with dilute sulfuric acid, boiled for 30 min, and allowed to stand in a refrigerator overnight. After removal of traces of grey powder the solution at pH 4.8 was evaporated on a hot plate until a large amount of white powder had separated. More product was obtained by cooling the solution slowly to room temperature. The crude product was dissolved in a minimum of lukewarm water and the pH adjusted to 4.8 with sodium hydroxide. The volume of the solution was reduced to ca. 30 ml by heating, and after cooling to room temperature the product was filtered off, washed with water and dried in the air. In most cases three or more recrystallizations were necessary to obtain a pure salt.

Hexamolybdobis-paminophenylarsonate, Guanidinium salt.--Par-aminophenylarsonic acid (2.2 g, 0.01 mol) and sodium hydroxide (2 g, 0.025 mol) were dissolved in ca. 100 ml of water and heated to boiling. To the boiling solution molybdenum trioxide (6.5 g, 0.045 mol) was added. The pH of the solution was adjusted to 4 with dilute sulfuric acid. Approximately 50 ml

of a pH 4 solution containing guanidinium hydrochloride (4.8 g, 0.05 mol) was added. The initial amorphous yellowish precipitate was filtered off and the solution left to evaporate. After several hours, shiny yellow needles mixed with some yellow microcrystalline powder precipitated out. The needles were mechanically separated from the powder and recrystallized from hot water at pH 4. The product was washed with cold water and dried in the air. The yield was 5 g, i.e. 62%. Tetramethylammonium salt. This salt was prepared in a similar fashion to the guanidinium salt described above.

Analyses.--Carbon, hydrogen, nitrogen, arsenic and molybdenum analyses were performed as described previously.<sup>7</sup>

Physical measurements.--Spectroscopic and electrochemical measurements were carried out as in our previous paper.<sup>7</sup>

Structure determination of  $[(CH_3)_4N]_2Na_2[(CH_3As)_4Mo_6O_{24}] \cdot 6H_2O$ .--A colorless crystal of approximate dimensions  $0.2 \times 0.3 \times 0.4$  mm was mounted on a glass fiber with the (1 0 1) direction coincident with the goniometer rotation axis. Precession photographs did not show any special symmetry or systematic absences, suggesting space groups  $C_1 - P\bar{1}$  or  $C_1^2 - P\bar{1}$ . A triclinic unit cell was assigned and a Delaunay reduction of the cell parameters failed to indicate any hidden symmetry. Cell dimensions were determined by a least squares refinement to fit the  $\pm 2\sigma$  values for 24 high-angle reflections centered on the

Picker FACS-I diffractometer. Crystallographic data are presented in Table II.

Integrated intensities were measured using Zr-filtered Mo  $K_{\alpha}$  radiation by the 0-2θ scan technique at a take-off angle of 1.5°. The peaks were scanned from 0.5° on the low-angle side of the  $K_{\alpha 1}$  peak to 0.5° on the high-angle side of the  $K_{\alpha 2}$  peak at a rate of 1.0°/min. Stationary crystal, stationary counter background counts of 10 s duration were taken at each end of the scan. The diffracted beams were counted using a scintillation counter and were automatically attenuated with zr foil whenever the count rate exceeded 8000 cps. A hemisphere of data (13766 reflections) was collected to  $2\theta = 50^\circ$ . The intensities of three standard reflections monitored after every 100 reflections, remained essentially constant. The intensities were corrected for background and standard deviations were estimated as previously described.<sup>8a</sup> The data were corrected for Lorentz and polarization effects and subsequently for absorption. Transmission coefficients ranged from 0.57 to 0.30. Only the 3175 unique reflections for which  $I \geq 2\sigma(I)$  were used in the solution and refinement of the structure.

A Patterson function was computed,<sup>9</sup> and the positions of the three crystallographically independent Mo atoms and the As atom in space group P1 were determined. Four cycles of least-squares refinement, assuming isotropic thermal parameters of  $1.5 \text{ \AA}^2$  for each atom, gave consistency indices  $R_1$  and  $R_2$  of

0.258 and 0.377 respectively, where  $R_1 = \Sigma(|F_O| - |F_C|)/\Sigma|F_O|$  and  $R_2 = (\Sigma(|F_O| - |F_C|)^2 / \Sigma|F_O|^2)^{1/2}$ . In this and succeeding refinements the function minimized was  $\Sigma w(|F_O| - |F_C|)^2$  where  $|F_O|$  and  $|F_C|$  are the observed and calculated structure amplitudes and where the weights,  $w$ , were taken as  $4F_O^2/\sigma^2(F_O^2)$ . The atomic scattering factors, including the anomalous terms for Mo and As, were taken from the usual tabulation.<sup>10</sup> A difference Fourier map gave the positions of all remaining non hydrogen atoms. Two cycles of isotropic least-squares refinement, followed by three cycles refining anisotropic thermal parameters for each atom in addition to the positional parameters, resulted in values of  $R_1 = 0.069$  and  $R_2 = 0.097$ . The intensities were next corrected for absorption, and two additional cycles of full-matrix refinement lowered the consistency indices to  $R_1 = 0.043$  and  $R_2 = 0.072$ . The standard deviation in an observation of unit weight was 2.5. A final difference Fourier map contained, as the most significant feature, a ring of electron density of  $0.5 \text{ e}/\text{\AA}^3$  in the vicinity of the expected positions of the methyl group hydrogen atoms of the anion. No attempt was made, however, to include hydrogen atoms in the model of the structure. The lack of residual electron density coupled with the successful structure refinement, supports the choice of the centric space group P1.

Table III presents the final positional and thermal parameters, along with the corresponding standard deviations. A table of the final values of  $|F_0|$  and  $|F_C|$  is available.

#### Results and Discussion

##### Description of the Structure

The structure consists of  $[(\text{CH}_3\text{As})_2\text{Mo}_2\text{O}_{10}]^{1-}$  anions,  $[\text{N}(\text{CH}_3)_3]^+$  cations, and  $\text{Na}^+$  cations coordinated by the water molecules to form  $[\text{Na}_2(\text{H}_2\text{O})_6]^{1+}$  dimers. Figure 1 presents a stereoscopic view of the contents of the unit cell. Both the  $[\text{Na}_2(\text{H}_2\text{O})_6]^{1+}$  dimers and the molybdate anion are located on inversion centers and are linked together through terminal oxygens on the anion to form a chain running along the  $\bar{a}$  axis. Selected bond distances and angles are given in Table IV. There are no unusually short nonbonded distances, the closest approach of anions being only 3.65 Å between O(9) and O(10). The water-anion distances range between 2.78 and 2.88 Å.

The  $\text{N}(\text{CH}_3)_3^+$  cation has the usual tetrahedral geometry with C-N-C angles ranging from 106.4 to 111.2°. The average N-C bond distance is 1.504 Å. The coordination geometry about the sodium dimer is that of two distorted octahedra sharing an edge. The sodium-water and sodium-oxygen distances, which range from 2.37 to 2.44 Å, correspond to those found in a similar cation described in a previous paper.<sup>8</sup>

A stereoscopic drawing of the  $[(\text{CH}_3\text{As})_2\text{Mo}_2\text{O}_{10}]^{1-}$  anion is presented in Figure 2. It is conveniently described as a fragment of a close packed oxide lattice with Mo atoms in

selected octahedral sites and two CH<sub>3</sub>As groups bound to its exterior surface through stable covalent bonds. Alternatively (see Figure 1) it may be viewed as six distorted octahedra joined together by edge sharing to form a flat metal oxide ring, which is capped, top and bottom, by the CH<sub>3</sub>As groups. This highly symmetrical anion exhibits approximately D<sub>3d</sub> symmetry. The metal oxide portion of the anion resembles the previously reported structures<sup>11</sup> of the heteropoly molybdates, (XMo<sub>6</sub>O<sub>21</sub>)<sup>n-</sup>. The average distances of 1.707, 1.919, and 2.351 Å for Mo-O(terminal), Mo-O(doubly-shared), and Mo-O(triply-shared) bonds compare favorably with those found in TeMo<sub>6</sub>O<sub>21</sub><sup>6-</sup>.<sup>12</sup> The geometry about the As is very close to tetrahedral with angles in the CH<sub>3</sub>AsO<sub>3</sub> group ranging from 106.9 to 111.8°. The As-C distance of 1.89 Å and the average As-O distance of 1.70 Å are consistent with values found in free organoarsenates.<sup>13</sup>

#### Solution Properties

On the preparative scale the alkyl- and arylarsanato-molybdate complexes are formed both with sodium molybdate and molybdenum trioxide in aqueous solutions at pH 4-5. In aqueous solutions of spectroscopic concentration (ca. 5 × 10<sup>-4</sup> M) though, they appear to be the predominant species in slightly more acidic media, i.e. pH 3-4. The analytical data for the complex salts are in good agreement with the empirical formula

$[(RAs)_2Mo_6O_{21}]^{n-}$  (Table I) and the structure determination also confirms this molecular stoichiometry.

The uv spectra of all three complexes have an absorption peak at about 250 nm. The electronic transition energy and the extinction coefficients are very close to the corresponding values for the  $[(RP)_2Mo_6O_{21}]^{n-}$  anions with extinction coefficients  $(3.5-5) \times 10^4 M^{-1} cm^{-1}$ .

From all the compounds reported by Rosenheim and co-workers,<sup>1</sup> only the salts formulated  $[C(NH_2)_2]_2[(2NH_2C_6H_5As)(MoO_4)_2] \cdot 5H_2O$  and  $[C(NH_2)_2]_2[(2HOC_6H_5As)(MoO_4)_2] \cdot 2H_2O$  appear to correspond to  $[(RAs)_2Mo_6O_{21}]^{n-}$ . No methyl derivative was reported. Although neither  $[(C_6H_5As)_2Mo_6O_{21}]^{n-}$  nor  $[(NH_2C_6H_5As)_2Mo_6O_{21}]^{n-}$  crystallizes easily with small inorganic cations such as Na<sup>+</sup>, K<sup>+</sup> and NH<sub>4</sub><sup>+</sup>, their quaternary ammonium salts can be relatively readily separated from the reaction solutions. Isolation of the tetramethyl-ammonium-sodium double salt of the  $[(CH_3As)_2Mo_6O_{21}]^{n-}$  anion proved to be more difficult. Compared to our previous syntheses of various salts of the  $[(RP)_2Mo_6O_{21}]^{n-}$ <sup>7</sup> and  $[(R_2As)_2Mo_6O_{18}H]^{2-}$ <sup>14</sup> anions, the preparation of the compounds reported here appears to be more sensitive to pH, temperature, precipitating conditions, concentration, etc., and isolation of pure crystalline material is time-consuming.

The infrared absorption spectra of all three complexes are

characteristic of the anion, and the main bands are listed in Table V.

The proton magnetic resonance spectrum of an analyzed sample of  $[(\text{CH}_3)_4\text{N}]_2\text{Na}_2[(\text{CH}_3\text{As})_2\text{Mo}_6\text{O}_{24}]\cdot 6\text{H}_2\text{O}$  in aqueous solution at pH 4 shows the anion methyl resonance at 2.20 ppm, about 0.30 ppm downfield from that of the free methyl arsonate anion under the same conditions. The ratio of the integrated intensities of the cation:anion methyl resonances was 4.2±0.2 and confirms the above stoichiometry. The slightly high value is probably a result of traces of  $(\text{CH}_3)_4\text{NCl}$  in the bulk sample rather than partial hydrolysis of  $\text{AsCH}_3$  to  $\text{AsOH}$  in the anion.

Polarography of  $5 \times 10^{-4}$  M solutions of the molybdoarsenate complexes at pH 3-4 revealed single irreversible waves at -0.6 to -0.7 V vs. sce, and indicates that the anions are not reducible to mixed valence, 'heteropoly blue' species. This behavior is consistent with the type II structure adopted by the complexes.<sup>15</sup>

Such a structure is compatible with the larger size of Sb(III) vis-a-vis As.

Complexes of molybdate and inorganic arsenate with the 1:3 stoichiometry are known. Contant<sup>20</sup> showed the existence of 2:6 and 4:12 anions, and Nishikawa and Sasaki<sup>21</sup> have recently determined the crystal structure of the ammonium salt of the latter complex. From potentiometric measurements,

#### Conclusions

The new complexes bear an obvious structural similarity to the 2:5 molybdophosphonate anions that we have reported previously.<sup>7,8</sup> In both structures a ring of  $\text{MoO}_6$  octahedra is spanned by  $\text{RKO}_3$  tripod groups, and the difference in stoichiometry appears to be dictated by the dimensions of  $\text{RPO}_4^{2-}$  and  $\text{RAsO}_4^{2-}$ . As we<sup>8</sup> and others<sup>4</sup> have independently pointed out, the appropriate O...O distances across the six-membered  $\text{Mo}_6\text{O}_{24}^{4-}$ -ring closely match the nonbonded O...O separation in an  $\text{AsO}_4^{3-}$ -tetrahedron (2.86 Å), whereas the smaller, buckled, edge- and corner-shared  $\text{Mo}_6\text{O}_{24}^{4-}$ -ring is needed to accommodate  $\text{PO}_4^{3-}$  or  $\text{RPO}_4^{2-}$  groups (0...O, 2.53 Å).<sup>16</sup> The structure of the  $\text{S}_2\text{Mo}_5\text{O}_{24}^{4-}$  anion<sup>17</sup> is consistent with this principle (O...O for  $\text{SO}_4^{2-}$  is 2.41 Å)<sup>18</sup> and it is probable that  $\text{Se}_2\text{Mo}_5\text{O}_{24}^{4-}$  (O...O, 2.61 Å)<sup>18</sup> has a similar structure. On the other hand the compound originally formulated as  $(\text{NH}_4)_4\text{Sb}_2\text{W}_5\text{O}_{24}\cdot \text{H}_2\text{O}$  has recently been shown<sup>19</sup> to contain an  $\text{Sb}_2\text{W}_{11}$ -structure based on fragments of a  $\beta$ -Keggin ( $\text{XW}_{12}$ ) molecule. Such a structure is compatible with the larger size of Sb(III) vis-a-vis As.

Table I.—Analytical Results for  $(\text{RAs})_2\text{Mo}_6\text{O}_{12}$ , Anhydrite

Pettersson<sup>22</sup> concluded that both 2:5 and 2:6 complexes of molybdate exist, the former in very small amounts, in aqueous solution at pH 3-6. Pettersson also proposed a structure for the 2:6 complex analogous to the one reported here. As mentioned above, Filowitz and Klemperer<sup>4</sup> showed that the  $^{17}\text{O}$  nmr spectra of  $(\text{OAs})_2\text{Mo}_6\text{O}_{4-}$  and  $(\text{C}_6\text{H}_5\text{As})_2\text{Mo}_6\text{O}_{4-}^{\cdot-}$  were consistent with the Pettersson structure.

In their original study Rosenheim and Billeck<sup>1</sup> reported the following compounds with a 1:3 stoichiometry:

[C(NH<sub>2</sub>)<sub>2</sub>]H[(C<sub>6</sub>H<sub>5</sub>As)(MoO<sub>4</sub>)<sub>2</sub>]; [C(NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>I[(PNH<sub>2</sub>C<sub>6</sub>H<sub>5</sub>As)(MoO<sub>4</sub>)<sub>2</sub>]<sub>2</sub>·H<sub>2</sub>O,  
and [C(NH<sub>2</sub>)<sub>2</sub>]<sub>2</sub>I[ph(C<sub>6</sub>H<sub>5</sub>As)(MoO<sub>4</sub>)<sub>2</sub>]<sub>2</sub>·2H<sub>2</sub>O. The last two salts  
almost certainly contain 2:6 anions of the type reported here.  
The first salt however is probably not an acid salt as written,  
but, we believe, contains a tetrmeric (4:12) anion analogous  
to the molybdoarsenate complex  $\text{I}(\text{HOAs})_4\text{Mo}_2\text{O}_{10}$ <sup>-</sup>. We have  
prepared several such derivatives and report them elsewhere. <sup>8b</sup>

Acknowledgment. The support of this research by the Office of Naval Research through Contract No. N00014-75-C-0945 is gratefully acknowledged.

TABLE II

## Crystal Data

Formula	$\text{Na}_2[\text{N}(\text{CH}_3)_4]_2[(\text{CH}_3\text{As})_2\text{Mo}_6\text{O}_{14}] \cdot 6\text{H}_2\text{O}$
Formula wt.	1441.92
a =	11.712(2) Å
b =	11.589(1) Å
c =	9.331(1) Å
a =	87.84(1)°
b =	110.31(1)°
y =	112.13(1)°
x =	21°C
z =	1
V =	976.6 Å³
$\rho_{\text{calc}}$ =	2.451 g/cm³
$\rho_{\text{obs}}$ =	2.45(2) g/cm³
$\nu$ =	37.29 cm⁻¹
$\lambda$ =	0.70926 Å

Crystal Faces: {010},\* {110}, {100},\* {011},\* {101}, {111}

\*Most prominent.

TABLE IV

Selected Distances (Å) and Angles (Deg) for  
 $\text{Na}_2[\text{N}(\text{CH}_3)_4]_2[(\text{CH}_3\text{As})_2\text{Mo}_6\text{O}_{14}] \cdot 6\text{H}_2\text{O}$ 

$[\text{N}(\text{CH}_3)_4]^+$		
<u>Atoms</u>	<u>Distance</u>	<u>Angle</u>
N-C(2)	1.502(11)	C(2)-N-C(3) 109.7(8)
N-C(3)	1.503(12)	C(2)-N-C(4) 106.4(8)
N-C(4)	1.520(11)	C(2)-N-C(5) 110.8(8)
N-C(5)	1.493(12)	C(3)-N-C(4) 108.2(7)
		C(3)-N-C(5) 111.2(8)
		C(94)-N-C(5) 110.4(8)
$\text{Na}^+(\text{aq})$		
<u>Atoms</u>	<u>Distance</u>	<u>Angle</u>
Na-Aq(1)	2.393(8)	Aq(1)-Na-O(9)* 83.6(2)
Na-Aq(2)	2.417(7)	Aq(2)-Na-Aq(2)* 80.4(2)
Na-Aq(2)*	2.371(7)	Aq(2)-Na-Aq(3) 81.6(2)
Na-Aq(3)	2.444(8)	Aq(2)-Na-O(6) 85.7(2)
Na-O(6)	2.392(7)	Aq(2)-Na-O(9)* 83.6(2)
Na-O(9)*	2.417(7)	Aq(2)-Na-Aq(3) 161.8(3)
		Aq(2)-Na-O(6) 95.5(2)
<u>Atoms</u>	<u>Angle</u>	
Aq(1)-Na-Aq(2)	162.6(3)	Aq(2)-Na-O(9)* 81.0(2)
Aq(1)-Na-Aq(2)*	85.9(3)	Aq(3)-Na-O(6) 80.5(3)
Aq(1)-Na-Aq(3)	112.2(3)	Aq(3)-Na-O(9)* 99.7(3)
Aq(1)-Na-O(6)	106.6(3)	O(6)-Na-O(9)* 169.1(3)
$[(\text{CH}_3\text{As})_2\text{Mo}_6\text{O}_{14}]^{2-}$		
Mo-Mo, As-Mo, and As-As Distances		
<u>Atoms</u>	<u>Distance</u>	<u>Atoms</u>
Mo(1)-Mo(2)	3.244(1)	As-Mo(1) 3.689(1)
Mo(2)-Mo(3)	3.300(1)	As-Mo(2) 3.646(1)
Mo(3)-Mo(1)*	3.290(1)	As-Mo(3) 3.640(1)
Mo(1)-Mo(3)	5.687(1)	As-Mo(1)* 3.691(1)
Mo(2)-Mo(1)*	5.689(1)	As-Mo(2)* 3.695(1)

TABLE IV - Continued

TABLE IV - Continued

<u>Atoms</u>	<u>Distance</u>	<u>Atoms</u>	<u>Atoms</u>	<u>Angle</u>
Mo (3)-Mo (2)*	5.655 (2)	As-Mo (3)*	O (3)-Mo (1)-O (4)	99.1 (2)
Mo (1)-Mo (1)*	6.571 (1)	As-As*	O (3)-Mo (1)-O (11)*	148.4 (2)
Mo (2)-Mo (2)*	6.527 (2)	As-As*	O (3)-Mo (1)-O (12)*	80.6 (2)
Mo (3)-Mo (3)*	6.568 (2)		O (4)-Mo (1)-O (11)*	87.8 (2)
			O (4)-Mo (1)-O (12)*	166.5 (2)
			O (11)-Mo (1)-O (12)*	74.4 (2)
			O (11)-Mo (1)-O (11)	0 (7)-Mo (3)-O (10)
			O (7)-Mo (3)-O (11)	149.6 (2)
			O (7)-Mo (3)-O (12)	0 (7)-Mo (3)-O (11)
			O (7)-Mo (3)-O (12)	80.7 (2)
			O (8)-Mo (3)-O (9)	82.4 (2)
			O (8)-Mo (3)-O (10)	0 (8)-Mo (3)-O (9)
			O (8)-Mo (3)-O (11)	166.5 (2)
			O (11)-Mo (1)-O (12)	0 (8)-Mo (3)-O (10)
			O (11)-Mo (1)-O (11)	0 (8)-Mo (3)-O (11)
			O (8)-Mo (3)-O (12)	74.8 (2)
			O (9)-Mo (3)-O (10)	105.5 (3)
			O (9)-Mo (3)-O (11)	95.2 (2)
			O (9)-Mo (3)-O (12)	161.1 (2)
			O (9)-Mo (3)-O (11)	149.7 (2)
			O (10)-Mo (3)-O (11)	101.3 (2)
			O (10)-Mo (3)-O (12)	79.9 (2)
			O (10)-Mo (3)-O (11)	91.7 (2)
			O (11)-Mo (3)-O (12)	92.3 (2)
			O (11)-Mo (3)-O (11)	163.1 (2)
			O (11)-Mo (3)-O (12)	74.7 (2)
			O (4)-Mo (2)-O (6)	80.4 (2)
			O (4)-Mo (2)-O (7)	
			1.931 (5)	
			1.912 (5)	
			1.909 (5)	
			1.925 (5)	
			1.905 (5)	
			1.931 (5)	

<u>Atoms</u>	<u>Distance</u>	<u>Atoms</u>	<u>Atoms</u>	<u>Angle</u>
Mo (1)-O (1)	1.709 (6)	Mo (1)-O (3)	O (3)-Mo (2)-O (4)	
Mo (1)-O (2)	1.698 (6)	Mo (1)-O (11)*	O (3)-Mo (2)-O (5)	
Terminal	Mo (2)-O (5)	Oxygen doubly shared by Mo (2)	O (3)-Mo (2)-O (6)	
Oxygen	Mo (2)-O (6)	1.719 (5)	O (4)-Mo (2)-O (5)	
	Mo (3)-O (9)	1.718 (5)	O (4)-Mo (2)-O (6)	
	Mo (3)-O (10)	1.713 (5)	O (4)-Mo (2)-O (7)	

<u>Atoms</u>	<u>Distance</u>	<u>Atoms</u>	<u>Atoms</u>	<u>Angle</u>
Mo (1)-O (4)	2.324 (5)	As-O (4)	C (1)-As-O (4)	
Mo (1)-O (12)*	2.358 (5)	As-O (8)*	C (1)-As-O (8)*	
Mo (2)-O (4)	2.284 (5)	As-O (12)	C (1)-As-O (12)	
Mo (2)-O (8)	2.398 (5)	As-C (1)	C (1)-As-O (12)	
Mo (3)-O (8)	2.433 (5)		1.890 (4)	
Mo (3)-O (12)	2.306 (5)			

<u>Atoms</u>	<u>Distance</u>	<u>Atoms</u>	<u>Atoms</u>	<u>Angle</u>
Oxygen triply shared by two Mo atoms and one As atom	Mo (1)-O (4)	1.711 (5)	O (4)-As-O (8)*	111.0 (3)
	Mo (1)-O (12)*	1.697 (5)	O (4)-As-O (12)	110.4 (2)
	Mo (2)-O (4)	1.695 (5)	O (8)*-As-O (12)	111.8 (2)
	Mo (3)-O (8)	2.433 (5)		
	Mo (3)-O (12)	2.306 (5)		

\*Primed atoms are related to the corresponding unprimed atoms by a center of symmetry.

<u>Atoms</u>	<u>Angle</u>	<u>Atoms</u>	<u>Angle</u>
O (1)-Mo (1)-O (2)	103.5 (3)	O (4)-Mo (2)-O (8)	74.6 (2)
O (1)-Mo (1)-O (3)	98.0 (2)	O (5)-Mo (2)-O (6)	104.7 (3)
O (1)-Mo (1)-O (4)	164.9 (2)	O (5)-Mo (2)-O (7)	97.6 (3)
O (1)-Mo (1)-O (11)*	99.7 (2)	O (5)-Mo (2)-O (8)	165.5 (2)
O (1)-Mo (1)-O (12)*	93.5 (2)	O (6)-Mo (2)-O (7)	101.1 (3)
O (2)-Mo (1)-O (3)	101.0 (3)	O (6)-Mo (2)-O (8)	89.4 (2)
O (2)-Mo (1)-O (4)	90.9 (2)	O (7)-Mo (2)-O (8)	75.9 (2)
O (2)-Mo (1)-O (11)*	98.6 (3)	O (7)-Mo (3)-O (8)	75.4 (2)
O (2)-Mo (1)-O (12)*	162.4 (2)	O (7)-Mo (3)-O (9)	102.4 (3)

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s, strong; m, medium; w, weak; b, broad; n, narrow; sh, shoulder

### C Tetraamethylammonium salt

Guanidium salt p

a Tetramethylammonium-sodium salt

$\text{C}_6\text{H}_5\text{Br}$	$\text{C}_6\text{H}_5\text{Cl}$	$\text{C}_6\text{H}_5\text{I}$	$\text{C}_6\text{H}_5\text{NH}_2$	$\text{C}_6\text{H}_5\text{NH}_2\text{Cl}$	Tertiary Amines	$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$	$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{Cl}$	$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{Br}$	$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{I}$	$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{NH}_2$	$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{NH}_2\text{Cl}$	$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{NH}_2\text{Br}$	$\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2\text{NH}_2\text{I}$	
1249 ( $\text{cm}^{-1}$ ) <sup>d</sup>	1083 ( $\text{cm}^{-1}$ )	1088 ( $\text{cm}^{-1}$ )	943 ( $\text{cm}^{-1}$ )	1092 ( $\text{cm}^{-1}$ )	1094 ( $\text{cm}^{-1}$ )	v (AS-C)	950 ( $\text{cm}^{-1}$ )	950 ( $\text{cm}^{-1}$ )	950 ( $\text{cm}^{-1}$ )	950 ( $\text{cm}^{-1}$ )	950 ( $\text{cm}^{-1}$ )	950 ( $\text{cm}^{-1}$ )	950 ( $\text{cm}^{-1}$ )	
922 ( $\text{s}$ )	930 ( $\text{s}$ sh)	928 ( $\text{w}$ )	890 ( $\text{s}$ )	891 ( $\text{s},\text{b}$ )	900 ( $\text{s}$ )	v (AS-O)	899 ( $\text{s}$ )	890 ( $\text{s}$ )	890 ( $\text{s},\text{b}$ )	910 ( $\text{s},\text{b}$ )	910 ( $\text{s},\text{b}$ )	910 ( $\text{s},\text{b}$ )	910 ( $\text{s},\text{b}$ )	
919 ( $\text{s}$ )														919 ( $\text{s}$ )
862 ( $\text{w}$ )														862 ( $\text{w}$ )
849 ( $\text{w}$ )														849 ( $\text{w}$ )
785 ( $\text{s},\text{b}$ )			794 ( $\text{s},\text{b}$ )	797 ( $\text{s},\text{b}$ )	795 ( $\text{s},\text{b}$ )									785 ( $\text{s},\text{b}$ )
822 ( $\text{s}$ )			825 ( $\text{s},\text{b}$ )	830 ( $\text{s},\text{b}$ )	840 ( $\text{s}$ )									822 ( $\text{s}$ )
797 ( $\text{s},\text{b}$ )														797 ( $\text{s},\text{b}$ )
667 ( $\text{s},\text{b}$ )														667 ( $\text{s},\text{b}$ )
655 ( $\text{s},\text{b}$ )														655 ( $\text{s},\text{b}$ )
665 ( $\text{s},\text{a}$ )														665 ( $\text{s},\text{a}$ )
675 ( $\text{s},\text{b}$ )														675 ( $\text{s},\text{b}$ )
657 ( $\text{s},\text{a}$ )														657 ( $\text{s},\text{a}$ )

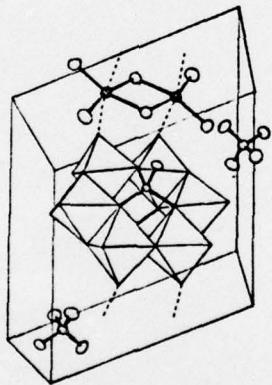
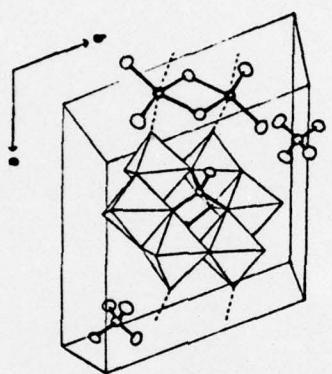
Table V. -Infrared Absorption Frequencies ( $\text{cm}^{-1}$ ) for  $(\text{RAs})_2\text{Mo}_6\text{O}_{24}$  Anilones

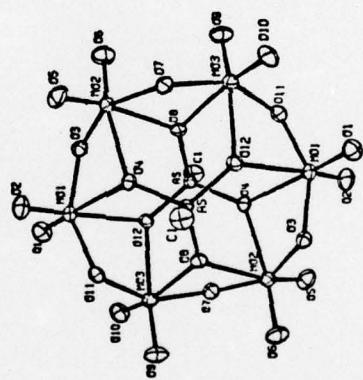
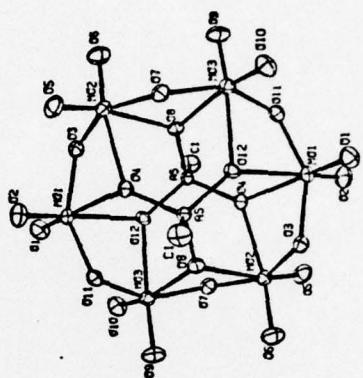
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Captions for Figures

Figure 1.--A stereoscopic view of the unit cell of  $\text{Na}_2[\text{N}(\text{CH}_3)_4]_2[(\text{CH}_3\text{As})_2\text{Mo}_6\text{O}_{24}] \cdot 6\text{H}_2\text{O}$ . The anions show  $\text{MoO}_6$  octahedra; all other vibrational ellipsoids are drawn at the 50% probability level. Sodium ions are shaded.

Figure 2.--A stereoscopic view of the  $[(\text{CH}_3\text{As})_2\text{Mo}_6\text{O}_{24}]^{4-}$  anion with vibrational ellipsoids drawn at the 50% probability level.





## Security Classification

## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author) Department of Chemistry Georgetown University Washington, D.C. 20057		2a. REPORT SECURITY CLASSIFICATION <u>unclassified</u>
2. REPORT TITLE <u>Synthesis and Structure of Hexamolybdo<b>bis</b>organoarsonates.</u>		
3. DESCRIPTIVE NOTES (Type of report and inclusive dates) <u>Technical Report</u>		
4. AUTHOR(S) (First name, middle initial, last name) <u>W. Kwak, L.M. Rajdovic, J.K. Stalick, M.T. Pope and C.O. Quicksall</u>		
5. REPORT DATE <u>November 1976</u>	7a. TOTAL NO. OF PAGES <u>27</u>	7b. NO. OF REFS <u>23</u>
6. CONTRACT OR GRANT NO. <u>N00014-75-C-0945</u>	9a. ORIGINATOR'S REPORT NUMBER(S) <u>Technical Report No. 6</u>	
7. PROJECT NO. <u>14 TR-6</u>	9b. OTHER REPORT NO(S) (Any other numbers that may be assigned this report)	
c.	10. DISTRIBUTION STATEMENT Approved for public release; distribution unlimited.	
11. SUPPLEMENTARY NOTES		12. SPONSORING MILITARY ACTIVITY Chemistry Branch Office of Naval Research Arlington, Va. 22217
13. ABSTRACT <p>Five salts of the heteropoly molybdate anion <math>(RAs)_2Mo_6O_{24}^4</math> (<math>R = CH_3, C_6H_5</math> and <math>p-C_6H_4NH_2</math>) have been synthesized and characterized by spectroscopic measurements. The complexes are stable in aqueous solutions at pH 3-5. The structure of <math>[(CH_3)_4N]_2Na_2[(CH_3As)_2Mo_6O_{24}] \cdot 6H_2O</math> (<math>P_1</math>; <math>a = 11.712(2)</math>, <math>b = 11.589(1)</math>, <math>c = 8.331(1)</math>, <math>\alpha = 87.84(1)^\circ</math>, <math>\beta = 110.31(1)^\circ</math>; <math>\gamma = 112.13(1)^\circ</math>) has been determined by single crystal X-ray diffraction. Final consistency indices of <math>0.043</math> (<math>R_1 = \sum( F_o  -  F_c )/\sum F_o </math>) and <math>0.072</math> (<math>R_2 = [\sum w( F_o  -  F_c )/\sum w F_o ^2]^{1/2}</math>) were obtained. The structure of the anion is closely related to that previously reported for <math>(CH_3P)_2Mo_5O_{21}^4</math> and consists of a ring of six edge-shared <math>MoO_6</math> octahedra capped above and below by the <math>CH_3AsO_3^-</math> groups.</p>		

14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Heteropoly complexes Organic derivatives Crystal structure Molybdoarsonates						